

## Some Physical Parameters of Calcium Chalcogenides at High Pressures: Semi-Empirical Approach

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Based on the experimental equations of state (EOS) of the parameters reported in the literature, in the present work, we reproduced the variation in the unit cell volume up to phase transition pressure for calcium-based chalcogenide CaX (X = S, Se, Te) semiconductor materials. We also studied the high-pressure effect on the crystal density, isothermal bulk modulus, the first order pressure derivative of the isothermal bulk modulus, and the Grüneisen parameter for CaX (X = S, Se, Te) binary compounds. It was found that, as the pressure increases, both the crystal density and the isothermal bulk modulus increase, while the first order pressure derivative of the bulk modulus and the Grüneisen parameter decrease gradually for all materials of interest. Similar behaviors of all these parameters against pressure were observed for several materials in the literature.

**Keywords:** Calcium chalcogenides, Grüneisen parameter, High pressure, EOS.

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### 1. INTRODUCTION

Alkaline-earth chalcogenides (AECs) form a very important closed-shell ionic system [1]. These binary compounds (AX: A = Be, Mg, Ca, Sr, Ba; X = O, S, Se, Te) are technologically important materials due to versatility in their physical properties, which make them useful for numerous applications such as microelectronics, luminescent devices, catalysis, etc. [2].

Except for beryllium chalcogenide compounds (which crystallize in the cubic zinc-blende or B3- phase) and some other binary materials, the majority of alkaline-earth chalcogenides crystallize in the NaCl-type (B1) structure at ambient conditions [3-5].

Among these AEC materials crystallized in the NaCl-type structure are calcium (Ca) based chalcogenides CaX (X = S, Se, Te). As all crystals, under high hydrostatic compression, the low-pressure phase of CaX (X = S, Se, Te) materials is destabilized, and the structural phase transition occurs [1]. For calcium sulfide (CaS), experience shows that the phase transition appears at a pressure of around 40 GPa; that for calcium selenide (CaSe) is at around 38 GPa, while for calcium telluride (CaTe), the first phase transition appears at a pressure of around 25 GPa [1].

Using first principles approach, Maizi et al. [6] have investigated the pressure dependence of the structural and elastic constants of cubic rock-salt CaX (X = S, Se, Te) compounds up to  $p = 30$  GPa. They have studied also the variation of the thermodynamic properties of CaX (X = S, Se, Te) with raising temperature up to  $T = 1200$  K.

M. Abdus Salam [7] has used an Ab initio calculation to study several physical properties of CaX (X = O, S, Se) alkaline-earth chalcogenide compounds. She

found that the indirect band gap  $E_{T-X}$  decreases as the nuclear charge of the anion increases.

Using the effective interionic interaction potential (EIoIP) with long-range Coulomb interactions and the Hafemeister and Flygare type short-range overlap repulsion (extended up to the second neighbor ions and the van der Waals interaction), Varshney and co-authors [8] have studied the pressure dependence of the Gibbs free energy, the second and third order elastic constants, and the Debye temperature of CaX (X = S, Se, Te) compounds. Their calculations on the structural phase transition revealed reasonably good agreement with the experimental data in the literature.

In the present work, we studied the high-pressure effect up to the phase transition on the variation in the relative unit cell volume  $- \Delta V/V_0$ , the crystal density  $\rho$ , the isothermal bulk modulus  $B$ , the first order pressure derivative of the isothermal bulk modulus  $B'$ , and the Grüneisen parameter  $\gamma$  of calcium-based chalcogenide CaX (X = S, Se, Te) semiconductor materials in the NaCl-type (B1) structure.

### 2. THEORY

There are several models [9-11] of the equations of state (EOS) relating the external pressure  $p$  and the relative volume  $(V/V_0)$  of a crystal under compression. Among these EOS models is the Vinet equation of state, which is expressed as follows [11]:

$$P(V) = 3B_0 \left[ \frac{1 - (V/V_0)^{1/3}}{(V/V_0)^{2/3}} \right] \exp \left\{ \frac{3}{2} (B_0' - 1) \left[ 1 - \left( \frac{V}{V_0} \right)^{1/3} \right] \right\}, \quad (1)$$

where  $B_0$  is the bulk modulus at ambient pressure,  $V$  is the volume of the solid at pressure  $p$ ,  $V_0$  is the unit cell

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volume at ambient pressure, and  $B'_0$  is the first-order pressure derivative of the bulk modulus  $B$  evaluated at ambient pressure (derivative of  $B$  with respect to  $p$ ).

If the lattice constants of any crystal are available, it is possible to calculate its crystal density  $\rho$ , using the general formula given as follows [12]:

$$\rho = \frac{Z M u}{abc(\sin^2 \alpha + \sin^2 \beta + \sin^2 \delta - 2(1 - \cos \alpha \cdot \cos \beta \cdot \cos \delta))^{1/2}}, \quad (2)$$

where  $Z$  is the number of formula units in a crystal unit cell,  $M$  is the molecular weight of a formula unit in amu,  $u$  is the weight of an amu,  $\alpha$ ,  $\beta$  and  $\delta$  are unit cell axes angles, while  $a$ ,  $b$ , and  $c$  are unit cell axes lengths.

According to the Vinet equation of state model, the isothermal bulk modulus  $B$  and the first order pressure derivative of the isothermal bulk modulus  $B'$  are respectively expressed as follows [13]:

$$B = B_0 x^{-2} [1 + (\eta x + 1)(1 - x)] \exp\{\eta(1 - x)\}, \quad (3)$$

$$B' = \frac{1}{3} \left[ \frac{x(1 - \eta) + 2\eta x^2}{1 + (\eta x + 1)(1 - x)} + (\eta x + 2) \right], \quad (4)$$

where  $x = \left(\frac{V}{V_0}\right)^{1/3}$  and  $\eta = \frac{3}{2}(B'_0 - 1)$ .

The Grüneisen parameter  $\gamma$  plays an important role in the study of the thermoelastic properties of materials. It helps in knowing the frequency distribution of the phonon spectrum in solids [13]. The Grüneisen parameter  $\gamma$  under compression may be calculated via Vashchenko-Zubarev formula as follows [14, 15]:

$$\gamma_{v-z} = \frac{\frac{1}{2} B' + \frac{2}{9} \left(\frac{p}{B}\right) - \frac{5}{6}}{\left(1 - \frac{4p}{3B}\right)}, \quad (5)$$

where  $B$  and  $p$  denote bulk modulus (incompressibility) and pressure at volume  $V$ .

### 3. RESULTS AND DISCUSSION

#### 3.1 Variation in the Relative Unit Cell Volume

In order to reproduce the variation in the relative volume  $-\Delta V/V_0 = -(V - V_0)/V_0$  of the unit cell for calcium-based chalcogenides CaX ( $X = S, Se, Te$ ) compounds under applied pressure  $p$ , we used the experimental EOS parameters reported by Luo et al. [1] (Table 1), which are measured at ambient pressure.

**Table 1** – EOS parameters of CaX ( $X = S, Se, Te$ ) measured at ambient pressure [1]

Parameter	CaS	CaSe	CaTe
$a_0$ (Å)	5.689	5.916	6.348
$B_0$ (GPa)	64	51	42
$B'_0$	4.2	4.2	4.3

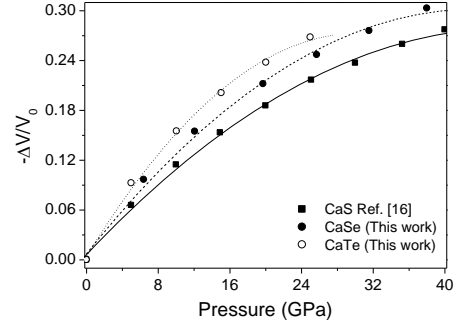
Fig. 1 discerns the variation of the relative volume ( $-\Delta V/V_0$ ) as a function of pressure  $p$  for CaX ( $X = Se, Te$ ) compounds in a cubic rock-salt structure, along

that of CaS material [16]. The fits of our data regarding  $-\Delta V/V_0$  as a function of  $p$  obey these expressions:

$$\frac{-\Delta V}{V_0} = 0.008 + 0.014p - 1.56 \times 10^{-4} p^2 \quad (\text{for CaSe}), \quad (6)$$

$$\frac{-\Delta V}{V_0} = 0.004 + 0.018p - 2.91 \times 10^{-4} p^2 \quad (\text{for CaTe}), \quad (7)$$

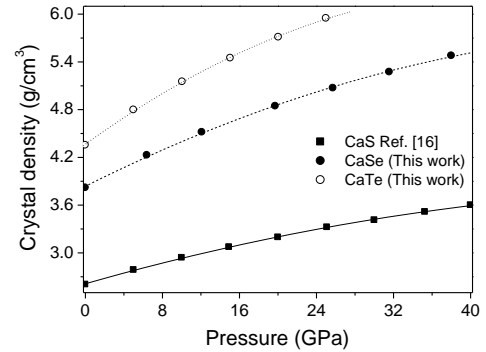
where  $p$  is expressed in GPa.



**Fig. 1** – ( $-\Delta V/V_0$ ) versus pressure  $p$  for CaX ( $X = Se, Te$ ) semiconductors, along that of CaS compound [16]

#### 3.2 Crystal Density

Attempting to predict the effect of pressure on the crystal density  $\rho$  for CaX ( $X = Se, Te$ ) compounds, the different results along that of CaS material [16] are presented in Fig. 2, which shows that crystal density  $\rho$  increases monotonically with applied pressure  $p$ .



**Fig. 2** – Crystal density as a function of pressure for CaX ( $X = Se, Te$ ) compounds, along that of CaS compound [16]

It is found from Fig. 2 that the variation of the crystal density  $\rho$  against pressure reported for CaSe and CaTe compounds is similar to those observed for other materials versus pressure as per literature [17-19].

The crystal density  $\rho$  (in  $\text{g/cm}^3$ ) against pressure  $p$  (in GPa) was fitted to the following second order polynomials:  $\rho = 3.84 + 6.06 \times 10^{-2} p - 4.68 \times 10^{-4} p^2$  for CaSe compound and  $\rho = 4.37 + 8.73 \times 10^{-2} p - 9.74 \times 10^{-4} p^2$  for CaTe, respectively.

Fig. 3 shows the variation of the isothermal bulk modulus  $B$  as a function of pressure for CaX ( $X = S, Se, Te$ ) compounds. As shown in Fig. 3, the isothermal bulk modulus  $B$  increases gradually with pressure for all our materials of interest, which can be explained by the fact that the bonding forces between atoms become stronger with increasing pressure.

A compound with relatively high compressibility is affected substantially more than that with relatively low compressibility. The fits of our data regarding the isothermal bulk modulus  $B$  as a function of  $p$  obey these expressions:

$$B = 64.26 + 3.964 p - 1.40 \times 10^{-2} p^2 \text{ (for CaS), (8)}$$

$$B = 51.47 + 3.848 p - 1.73 \times 10^{-2} p^2 \text{ (for CaSe), (9)}$$

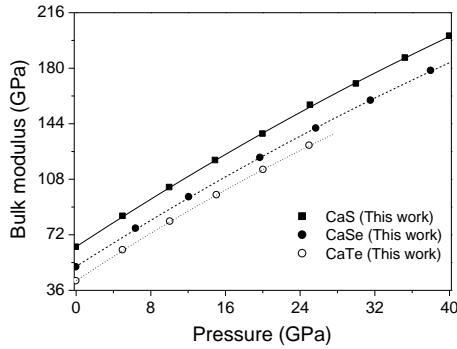
$$B = 42.22 + 4.007 p - 2.04 \times 10^{-2} p^2 \text{ (for CaTe), (10)}$$

where both  $B$  and  $p$  are expressed in GPa.

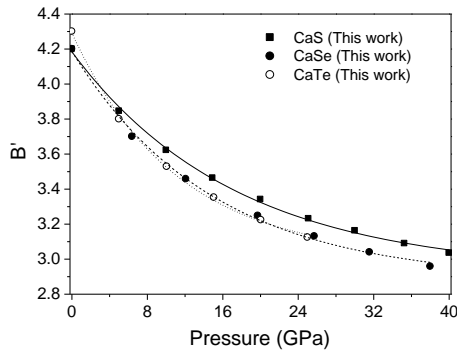
At zero pressure, as well as at high pressures, the bulk modulus  $B$  of CaS is greater than these of CaSe and CaTe compounds. Hence, we can conclude that CaS material is more incompressible than CaSe and CaTe.

It can be noted that a similar qualitative behavior of the isothermal bulk modulus  $B$  versus pressure has been reported for AlP semiconductor in zincblende (B3) phase [12] and MgCa in CsCl-type (B2) phase [19].

The plots of the first order pressure derivative of the isothermal bulk modulus  $B'$  versus pressure for CaX ( $X = S, Se, Te$ ) are shown in Fig. 4.



**Fig. 3** – Isothermal bulk modulus  $B$  against pressure for CaX ( $X = S, Se, Te$ ) compounds



**Fig. 4** – First order pressure derivative of the isothermal bulk modulus versus pressure for CaX ( $X = S, Se, Te$ ) compounds

Such as the volume,  $B'$  decreases also monotonically with raising pressure for all our materials of interest. The best fits of our data regarding the first order pressure derivative of the isothermal bulk modulus  $B'$  as a function of  $p$  obey these exponential expressions:

$$B' = 2.93 + 1.26 \exp(-p/17.34) \text{ (for CaS), (11)}$$

$$B' = 2.88 + 1.31 \exp(-p/14.88) \text{ (for CaSe), (12)}$$

$$B' = 3.01 + 1.29 \exp(-p/11.04) \text{ (for CaTe), (13)}$$

where  $B'$  is dimensionless and  $p$  is expressed in GPa.

Additionally, three linear analytical relations for the pressure dependence of  $B'$  for CaX ( $X = S, Se, Te$ ) compounds may be deduced from the derivation to respect the pressure ( $B' = \partial B / \partial p$ ) of  $B$ , i.e., from the derivation of Eqs. (8), (9) and (10):

$$B' = 3.964 - 2.80 \times 10^{-2} p \text{ (for CaS), (14)}$$

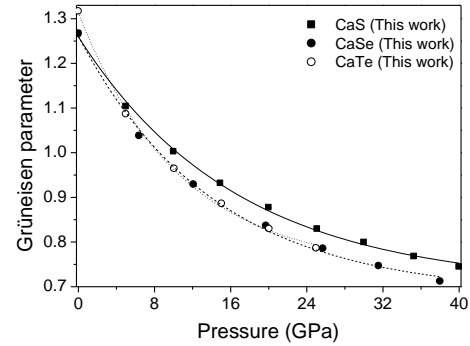
$$B' = 3.848 - 3.46 \times 10^{-2} p \text{ (for CaSe), (15)}$$

$$B' = 4.007 - 4.08 \times 10^{-2} p \text{ (for CaTe), (16)}$$

where  $B'$  is dimensionless and  $p$  is expressed in GPa.

To the best of the authors' knowledge the pressure dependence of  $B'$  has never been previously reported in the literature for CaX ( $X = S, Se, Te$ ) compounds.

Fig. 5 shows the variation of the Grüneisen parameter  $\gamma$  as a function of pressure for CaX ( $X = S, Se, Te$ ) compounds.



**Fig. 5** – Grüneisen parameter versus pressure for CaX ( $X = S, Se, Te$ ) compounds

As shown in Fig. 5, it is very clear that  $\gamma$  decreases monotonically with increasing pressure  $p$  for all materials of interest. The Grüneisen parameters  $\gamma$  of CaS, CaSe and CaTe materials start with the values of 1.27, 1.27, and 1.32, respectively at zero pressure, and they reach the values of 0.74, 0.71, and 0.79 at 40, 38, and 25 GPa, respectively.

The best fits of our data on the Grüneisen parameter  $\gamma$  as a function of pressure obey the following exponential expressions:

$$\gamma = 0.703 + 0.557 \exp(-p/16.61) \text{ (for CaS), (17)}$$

$$\gamma = 0.683 + 0.558 \exp(-p/14.21) \text{ (for CaSe), (18)}$$

$$\gamma = 0.739 + 0.574 \exp(-p/10.61) \text{ (for CaTe), (19)}$$

where  $\gamma$  is dimensionless and  $p$  is expressed in GPa.

Similar qualitative behavior of  $\gamma$  versus pressure has been reported for bulk and nano ZnO materials in both B4 and B1 phases [13].

Several works calculate the Debye temperature  $\theta_D$  of solids from the elastic constants [8, 19-22]. Usually,  $\theta_D$  decreases with increasing temperature and increases with increasing pressure [8]. The value of  $\theta_D$  can be determined with high precision from low-temperature measurements of the specific heat [19]. The Debye temperature  $\theta_D$  of several ionic compounds is adjusted to the bulk modulus  $B$  as follows [16, 22]:

$$\theta_D = (\hbar / k_B)(5r_0 B / \mu)^{1/2}. \quad (20)$$

Here  $\hbar = h/2\pi$ ,  $h$  is the Planck constant,  $r_0$  is the nearest-neighbor distance,  $k_B$  is the Boltzmann constant, and  $\mu$  is the reduced mass. The number 5 applies only to crystals with a NaCl-type structure [16, 22]. By substituting the experimental values reported by Luo et al. [1] of  $r_0$  and  $B$  into Eq. (20), the values of  $\theta_D$  were found to be 315.7 K for CaSe and 277.1 K for CaTe, respectively. Our values of  $\theta_D$  are in very good agreement with the theoretical ones  $\sim 327$  and  $\sim 260$  K reported by Varshney et al. [8].

#### 4. CONCLUSIONS

In conclusion, we determined the effect of high pressure on the crystal density, isothermal bulk modu-

lus, first order pressure derivative of the isothermal bulk modulus, and the Grüneisen parameter for CaX (X = S, Se, Te) binary compounds, followed by several analytical expressions established for these materials.

In comparison with other previous works, similar qualitative behaviors of all these parameters versus pressure have been reported for several materials in different structures.

To the best of the authors' knowledge the pressure dependence of the first order pressure derivative of the isothermal bulk modulus and the Grüneisen parameter has never been previously reported in the literature for CaX (X = S, Se, Te) compounds. So, in view of the limited experimental and theoretical values no valuable comparison has been made and we suggest that our data are predictions to be verified by future experiments or other theoretical approaches.

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### Деякі фізичні параметри халькогенідів кальцію при високих тисках: напівемпіричний підхід

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Базуючись на експериментальних рівняннях стану, наведених у літературі, у роботі ми відтворили зміну об'єму елементарної комірки залежно від тиску фазового переходу для халькогенідних напівпровідникових матеріалів CaX (X = S, Se, Te) на основі кальцію. Ми також досліджували вплив високого тиску на густину кристалів, ізотермічний модуль об'ємної деформації, похідну першого порядку за тиском від ізотермічного модуля об'ємної деформації та параметр Грюнаїзена для бінарних сполук CaX (X = S, Se, Te). Було виявлено, що зі збільшенням тиску густина кристала та ізотермічний модуль об'ємної деформації збільшуються, тоді як похідна першого порядку за тиском від модуля об'ємної деформації та параметр Грюнаїзена поступово зменшуються для всіх досліджуваних матеріалів. Подібна поведінка всіх цих параметрів залежно від тиску описана в літературі для кількох матеріалів.

**Ключові слова:** Халькогеніди кальцію, Параметр Грюнаїзена, Високий тиск, EOS.